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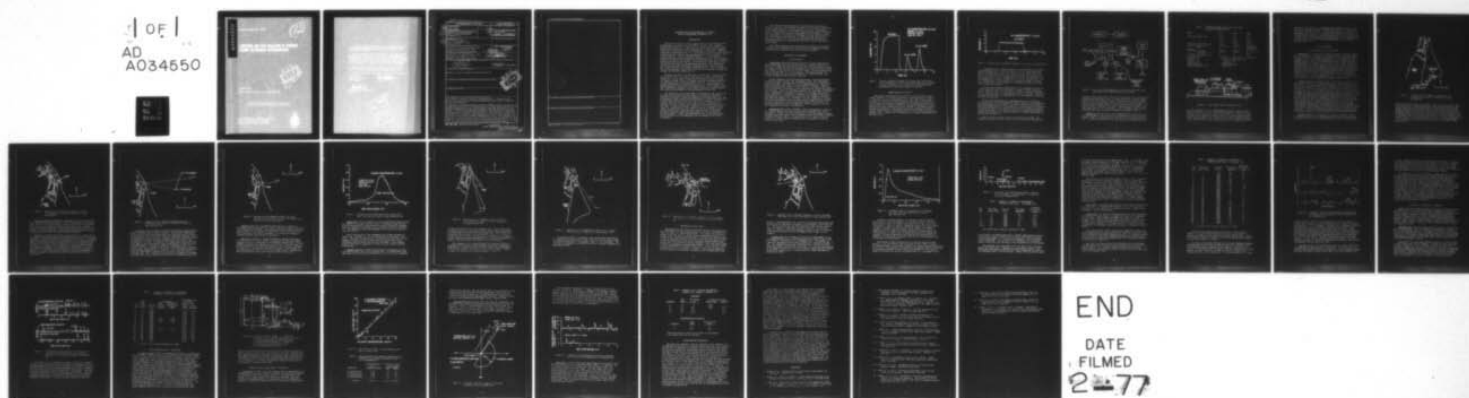
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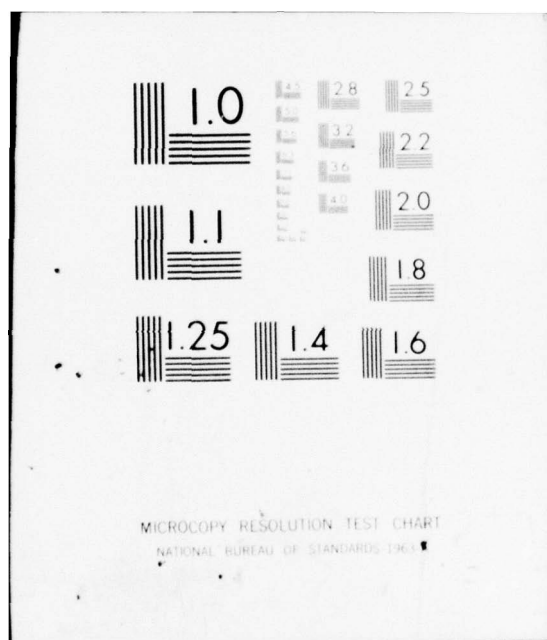
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# LABORATORY AND FIELD EVALUATION OF HYDROGEN CHLORIDE MEASUREMENT INSTRUMENTATION

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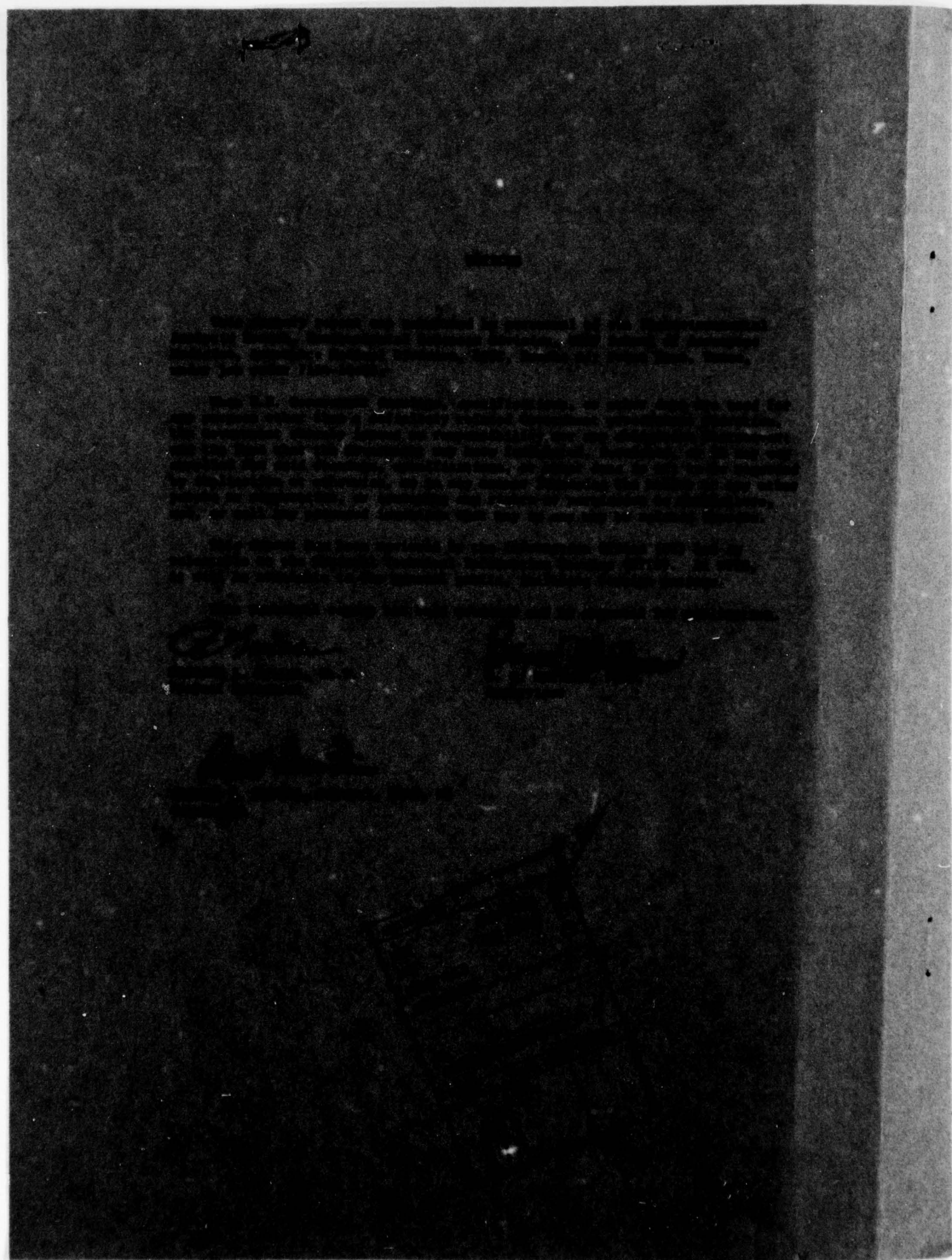
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USAF SCHOOL OF AIRCRAFT ENGINEERING  
Aerospace Medical Division (AFM)  
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

## LABORATORY AND FIELD EVALUATION OF HYDROGEN CHLORIDE MEASUREMENT INSTRUMENTATION

### INTRODUCTION

The Titan III series of space launch vehicles was developed by the United States Air Force in the mid 1960's to insert large unmanned payloads into space orbit. The Titan III system develops greater than 2 million pounds thrust at liftoff using two solid rocket motor segments (stage zero) containing a total of 870,000 lbs of propellant. The solid propellant formulation consists of a polybutadiene-acrylic acid-acrylonitrile binder mixed with aluminum fuel and ammonium perchlorate oxidizer. The liquid propellants used in subsequent stages--1, 2, and 3--are the standard nitrogen tetroxide oxidizer and Aerozene-50 fuel (50% by weight mixture of hydrazine and unsymmetrical dimethylhydrazine) used in numerous liquid rocket motor applications. Solid propellant formulations used in the initial stage lead to the generation of several toxic exhaust constituents in the lower atmosphere, including hydrogen chloride (HCl) gas, carbon monoxide, and aluminum oxide particulate. This contribution has in turn generated considerable study into the atmospheric mixing and ultimate fate of these chemicals (3).

Hydrogen chloride is the most toxic of three main solid propellant effluents, and hence the exhaust constituent of primary environmental concern (8). In the early studies on environmental effects of large solid motor firings, HCl in the exhaust cloud was determined by bubbler air sampling and wet chemistry analysis (2,17,18). This procedure proved only marginally successful due in part to sample averaging and, perhaps mainly, to difficulties in sample siting. Later attempts at a more comprehensive sampling network using pH-sensitive papers provided only qualitative estimates of the acid exposure profile (9).

The USAF School of Aerospace Medicine (USAFSAM) became involved in HCl monitoring by extension of previous work involving continuous analysis of chlorine in chemically generated breathing oxygen (14), and we developed a highly sensitive microcoulometer to detect sub-ppm (50 to 80 ppb) concentrations of chlorine. Since the coulometer, in fact, converts dissolved chlorine to chloride ion prior to detection, it required only minor modification to adapt the instrument system to HCl detection. Following laboratory validation of the coulometric technique, the instrument was field tested at several locations in cooperative programs with other Air Force organizations, the National Aeronautics and Space Administration (NASA), and the Environmental Protection Agency. These tests demonstrated that the microcoulometer was an excellent tool for measuring total HCl dosage in the static environment.



The airborne monitoring program at Vandenberg Air Force Base, however, required a fast-response instrument to determine instantaneous concentration changes in a short-exposure situation. Following an earlier NASA program (5) the USAFSAM contracted with Geomet Corporation, Pomona, California to develop a chemiluminescent-HCl analyzer to meet this requirement. The resulting instrument (16) was field tested in a June 1975 airborne monitoring test at Vandenberg AFB, and has been subsequently used by the Air Force Rocket Propulsion Laboratory in assessing downwind HCl concentrations from static test of the MX prototype engine.

This report describes the operating characteristics of the microcoulometric and chemiluminescent HCl analyzers and summarizes results from the several laboratory and field evaluation studies.

## DESCRIPTION OF EQUIPMENT

### Microcoulometer

Description--The microcoulometer we used for both ground and airborne monitoring of HCl has been described in a previous report (15). Briefly, the basis for the technique is chloride precipitation by silver ion, which is electrolytically replenished at a cost in electric current proportional to the chloride ion (or HCl) dosage. Because Faraday's law applies and the reaction is stoichiometric, the microcoulometer is a primary standard for chloride determination in liquid solution. The threshold detection limit is about 3 ng (15).

In the continuous air-monitoring application, the microcoulometer is limited in both response time and dynamic range. The combination largely precludes a determination of HCl concentration for steady-state exposures of more than 5 ppm for less than about 8 seconds. Figure 1 helps illustrate the problems. In the (typical) non-steady state field situation, the HCl concentration can be estimated for certain concentration-time profiles. Since the instrument response time (lag time) is approximately compensated by instrument overshoot, the average concentration can be estimated by assuming HCl is admitted only during titration rise. Measurement of the titration peak area gives total weight of chloride from which HCl volume can be calculated. Average concentration is then obtained by dividing HCl volume by the volume of sample admitted during the time interval from initial instrument response to peak apex. In laboratory experiments, this procedure has proved accurate to  $\pm 10\%$  for short exposures of constant concentration.

Calibration--The unique advantage of the microcoulometer is that it is a primary standard and thus does not require multiple point field calibration. We have routinely standardized the microcoulometer in both laboratory and field tests using a standard solution containing 20 mg/liter of sodium chloride in water. Syringe injection of 5 and 10  $\mu$ l of the standard at a given range setting generates a reproducible titration curve of known dosage.



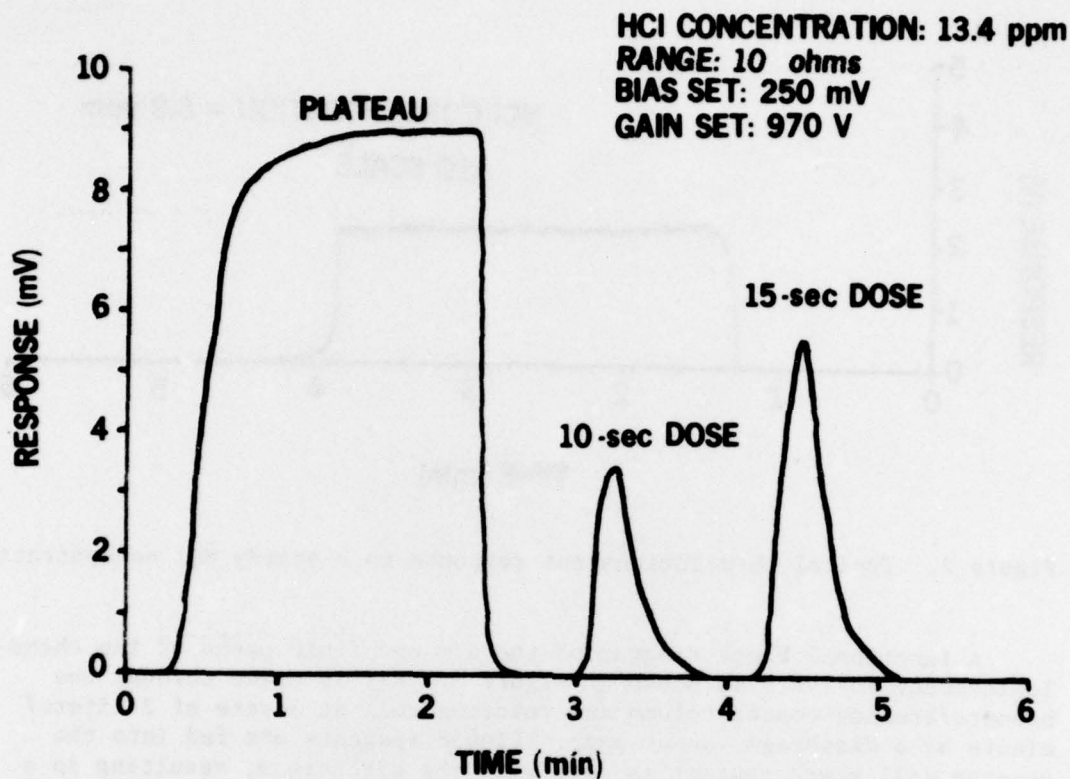


Figure 1. Typical coulometric response to a steady HCl concentration. (The combination of a high concentration and a slow response prohibits attainment of a plateau and thus concentration determination in the short exposure situation.)

#### Chemiluminescent Analyzer

Description--Chemiluminescent detection of HCl is based on exothermic oxidation of 5-amino-2,3-dihydro-1,4-phthalazinedione (luminol) in alkaline solution by hypochlorous acid. The light intensity generated by this reaction is linearly proportional to HCl concentration in the incoming gas stream and is measured by a photomultiplier detector. Hypochlorous acid is formed from HCl by passing the incoming air stream through an alumina column coated with a solution of 10% sodium bromate and 10% sodium bromide. This mixture reacts with hydrogen chloride to produce hypochlorite and hypobromite which initiate luminol oxidation to generate light. Figure 2 is a reproduction of a typical chemiluminescent analyzer output.

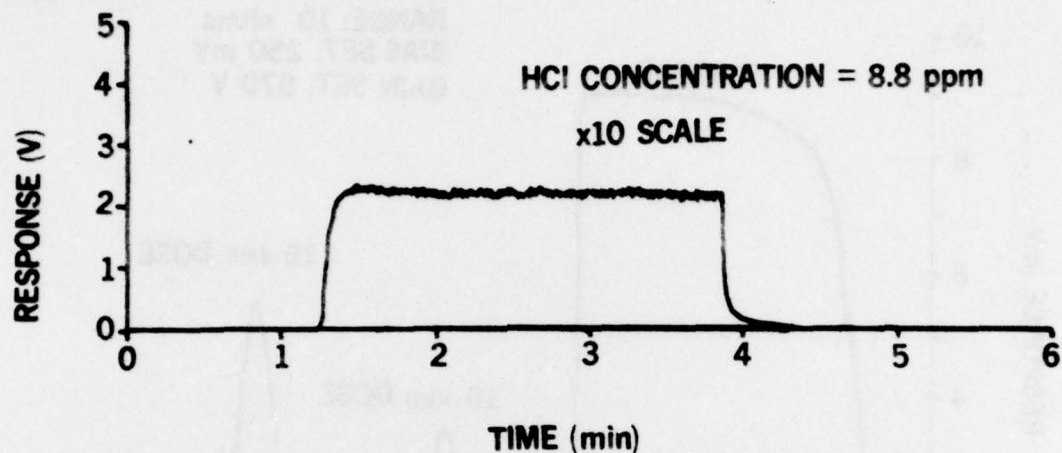


Figure 2. Typical chemiluminescent response to a steady HCl concentration.

A functional block diagram of the air and fluid paths of the chemiluminescent analyzer is shown in Figure 3. Air is drawn through the bromate/bromide-coated column and reaction cell at a rate of 2 liters/minute by a diaphragm vacuum pump. Liquid reagents are fed into the reactor cell where contact is made with the air stream, resulting in a chemiluminescence intensity proportional to the HCl concentration. The air-reagent mixture is then pumped into a reservoir where the liquid waste is deposited. The effluent gas is exhausted through a flow regulation valve and flowmeter.

The two liquid reagents employed are (a) 0.3% hydrogen peroxide in 0.086% phosphoric acid, and (b) luminol (2 mg/ml) in 0.5M sodium carbonate. Both reagents are stable and are stored in separate reservoirs in the instrument case. The reagents are metered in separate lines by a constant speed-peristaltic pump and mixed in a tee immediately upstream from the reaction cell.

We have used three models of chemiluminescent HCl analyzers in various studies; all were developed by Geomet Corporation and embody the same luminol detection principle. The first instrument (Geomet Model 401) was designed primarily for laboratory use and contained two reaction cells, one for detection of HCl and the other for reference subtraction of interferent gases. The reference cell inlet is an uncoated alumina column, and was found to be mainly sensitive to chlorine interference in chlorine-HCl mixtures (5).

Because of the relative bulk of the laboratory instrument, the USAFSAM contracted with Geomet Corporation in late 1974 to develop two

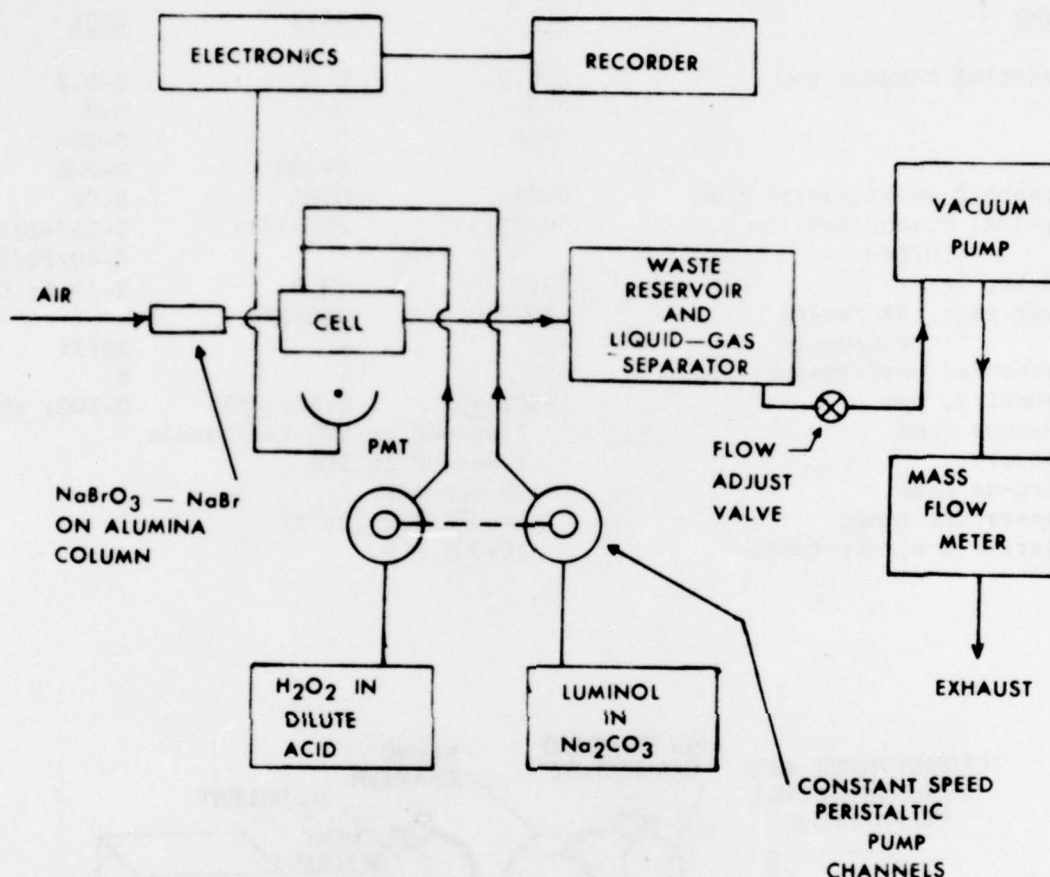


Figure 3. Functional block diagram of the air and fluid paths in the Geomet Model 402B chemiluminescent HCl monitor.

improved chemiluminescent-HCl analyzers for different field applications--ground and airborne monitoring. The improved ground instrument (Model 401B) is about one-fourth the size of the Geomet Model 401 and weighs only 13 kg (30 lb), making it easily portable for field deployment. The airborne monitor (Model 402B) is a split instrument with separate control and sensor components, for ease of installation in aircraft. The 402B is designed for 28 VDC operation. The performance specifications for Models 401, 401B, and 402B instruments are shown in Table 1.

Calibration--Calibration of the chemiluminescent HCl monitors has been accomplished in the laboratory by standardization with a microcoulometer. Figure 4 illustrates the setup used in the calibration procedure. A steady concentration of HCl gas is passed simultaneously into



TABLE 1. PERFORMANCE SPECIFICATION FOR THE GEOMET  
HYDROGEN CHLORIDE MONITORS

Model	401	401B	402B
Operating ranges, ppm	0-0.5 0-5 0-50	0-0.1 0-1 0-10 0-100	0-0.2 0-2 0-20 0-200
Threshold sensitivity, ppm	0.05	0.01	0.02
Physical dimensions, cm	50/70/35	22/37/25	S-25/46/20 C-40/23/10
Weight, kg	22.7	13.5	S-13.6; C-4.5
Power req. VAC/watts	110/250	110/250	-
VDC/watts	-	-	28/75
Unattended performance, hr	8	4	6
Linearity, ppm	0-50, $\pm 5\%$	0-50; $\pm 5\%$	0-100; $\pm 5\%$
Response time	1 second to 90% full scale		
Recovery	1 second to 10%		
Start-up time	10 minutes		
Temperature range	0-40°C (32-104°F)		
Relative humidity range	10-95% R.H.		

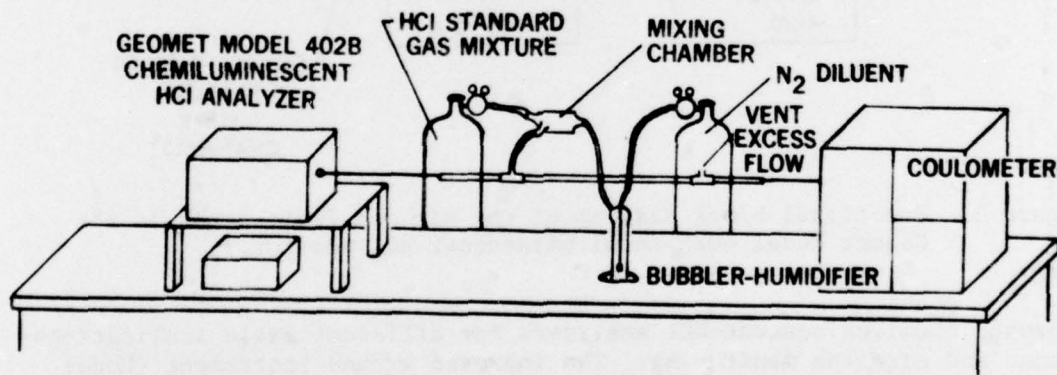


Figure 4. Geomet (Model 402B) calibration setup.

both the coulometer and the chemiluminescent analyzer under a slight positive pressure. When the steady-state response is achieved by the coulometer, the concentration may be calculated (15) and used to adjust the span on the chemiluminescent analyzer. We have used HCl gas mixtures produced commercially in pressurized cylinders, and also produced in the laboratory by passing nitrogen gas over a diffusion tube in a



calibration oven (Analytical Instruments Development Model 309). The diluent nitrogen may be passed through a water bubbler to humidify the gas prior to addition of HCl. A low relative humidity inhibits the chemiluminescent reaction by drying the bromate-bromide coating in the column and thus slowing the hypochlorite/hypobromite-producing reaction. In field tests, the chemiluminescent analyzer has been calibrated in the laboratory before and after each field measurement, with acceptable reproducibility (12).

## FIELD EVALUATION

### Cape Canaveral Air Force Station

Background--In mid-1972 the National Aeronautics and Space Administration initiated a comprehensive program of monitoring space launch vehicle effluents in response to and support of the Final Environmental Statement for the Space Shuttle program (4). At the request of the Langley Research Center, the USAFSAM participated in the tropospheric (ground) monitoring portion of this project. The primary objective of the program was to obtain field data for validation of the multilayer dispersion model employed by NASA to predict the behavior of launch vehicle ground exhaust. Measurement systems employed by NASA included detectors for hydrogen chloride, carbon monoxide, carbon dioxide, and aluminum oxide particulate. The USAFSAM participation involved our microcoulometric detectors for measurement of total chloride in the surface exhaust clouds. We participated in a total of eight monitoring tests during the period November 1972 through September 1975.

November 1972--On 9 November 1972, a Delta-Thor rocket launch was monitored for detection of HCl and particulate concentration in the ground cloud. HCl measurements were conducted by three microcoulometers (and several bubblers) at sites shown in Figure 5. The Delta launch occurred at 2014 hours from launch complex-17 (LC-17) at Cape Canaveral Air Force Station. The coulometers at sites "R" and "S" were operated by USAFSAM personnel while the coulometer at "MAML" was unmanned. NASA personnel deployed mass-monitoring instrumentation at sites "R" and "S." No other instrumentation was deployed. Continuous monitoring of the three coulometers showed no quantifiable detection of HCl in the atmosphere during or after launch, attributed in part to the fact that the predicted maximum HCl concentration at the "S" site was 0.075 ppm ( $0.12 \text{ mg/m}^3$ ) which was below the threshold sensitivity of 0.08 ppm ( $0.13 \text{ mg/m}^3$ ). Additionally, a wind shift, which occurred shortly before launch, placed the coulometers at the outside edge of the actual cloud trajectory. Particulate measurements made by NASA, however, showed cloud arrival almost exactly in accordance with model prediction (10).

December 1973--On 13 December 1973, two microcoulometers were deployed, along with a full complement of NASA monitoring instruments for launch of a Titan IIIC at Cape Canaveral (LC-40). Because of the

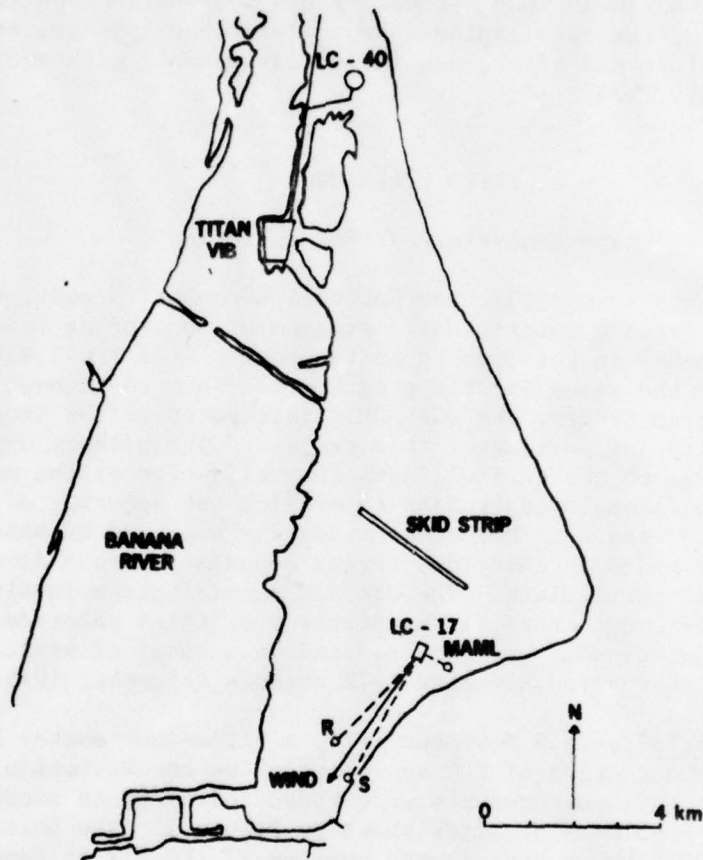


Figure 5. Sampling sites of USAFSAM coulometers for the 9 November 1972 launch of a Delta-Thor at Cape Canaveral AFS.

predicted (seaward) path of the exhaust cloud and the issuance of small-craft advisories, all measurements were confined to land in the area between the launch pad and approximately 2 km downwind (Fig. 6). The microcoulometers were deployed in the so-called fallback zone and were unmanned 3 hours before launch to approximately 1 hour after launch. No measurable effluents were recorded by either the microcoulometers or any of the NASA gaseous or particulate monitoring systems (6). White particles found on top of the microcoulometer case at site FF indicated that at least a portion of the buoyant exhaust cloud passed overhead of that monitoring site.

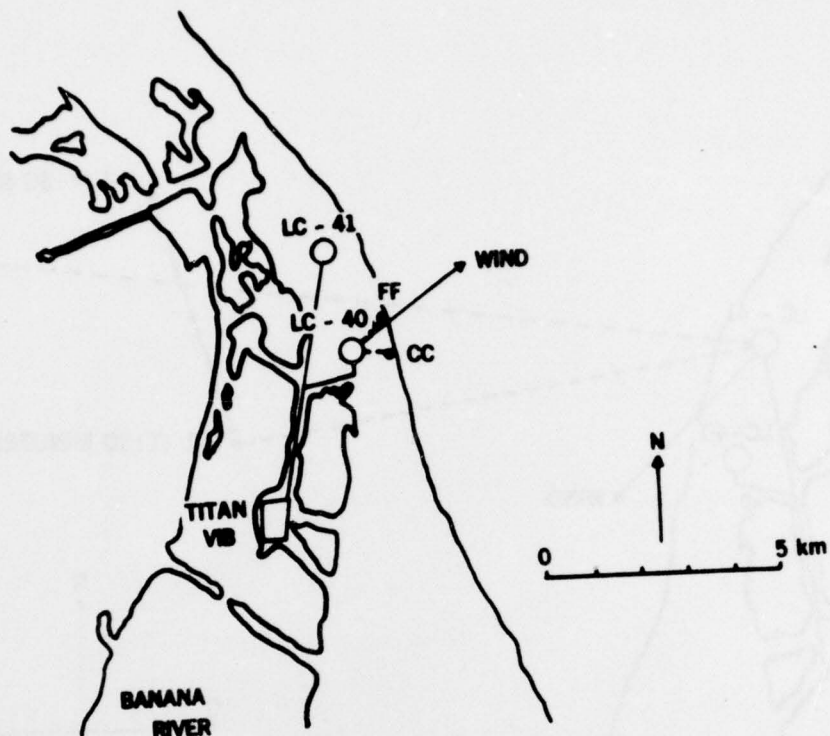


Figure 6. Sampling sites of USAFSAM coulometers for the 13 December 1973 launch of a Titan IIIC at Cape Canaveral AFS.

February 1974--Microcoulometric measurements for ground-level HCl were conducted during the launch of a Titan IIIE-Centaur on 11 February 1974. Because of capricious winds, no HCl was detected by the coulometers nor any of the NASA HCl detection instruments (19). Figure 7 shows the sampling positions of the HCl monitors employed for this test. Actual cloud travel was south of the deployed monitoring ships and did not make contact with any of the monitoring instruments.

May 1974--Downwind effluent HCl was detected for the first time in the NASA/AF monitoring program, following launch of a Titan IIIC vehicle from LC-40, Cape Canaveral Air Force Station on 30 May 1974. The USAFSAM monitoring equipment included a microcoulometer and a chemiluminescent analyzer (Geomet Model 401), both deployed on an ocean tugboat at site P-2 (Fig. 8). Figure 9 shows a reproduction of the response obtained with the microcoulometer. The average HCl concentration of 1.8 ppm ( $2.9 \text{ mg/m}^3$ ) was obtained at T+22.8 minutes at the position indicated on Figure 8. The detection time was confirmed by the chemiluminescent detector although its pulsed-type response largely negated accurate quantitation.



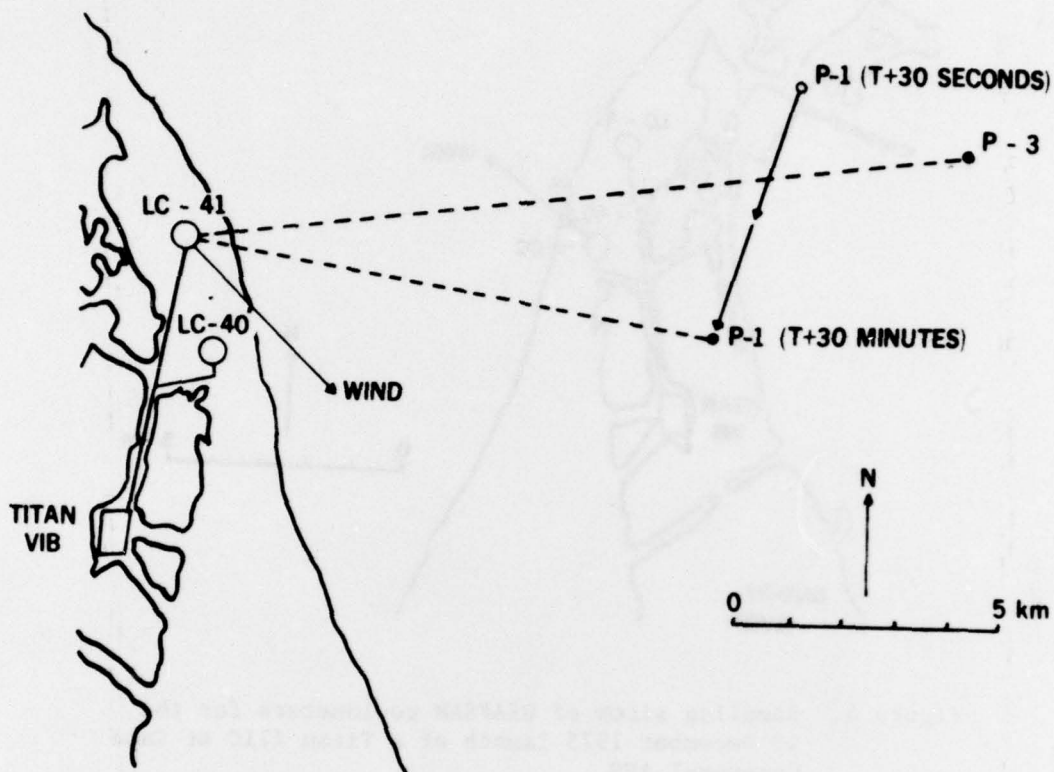


Figure 7. Sampling sites of USAFSAM coulometers for the 11 February 1974 launch of a Titan IIIE-Centaur at Cape Canaveral AFS.

The tugboat (P-2) arrived at its prelaunch holding position approximately 5 km from LC-40 at about T-2 hours. This position, immediately north of the boat-hit-probability-contour, was maintained until launch. At T+4 minutes, P-2 headed south toward its preassigned sampling location. Concurrent with launch, however, a southerly wind shift was detected and the vessel was vectored in a more southeasterly direction for cloud interception. At about T+19 minutes, the tugboat made contact with the outer edge of the moving exhaust cloud, approximately 5.2 km from LC-40 on an 81° azimuth. During the estimated cloud passage time of 1.9 minutes, the total HCl dosage was 454 ng (as chloride) which calculated to an average concentration of 1.8 ppm HCl. This concentration was well below the time-weighted average short-term public limit of 4 ppm for 10 minutes (8). The average HCl concentration was estimated by assuming the total chloride dose was admitted during the 1.9-minute passage time.



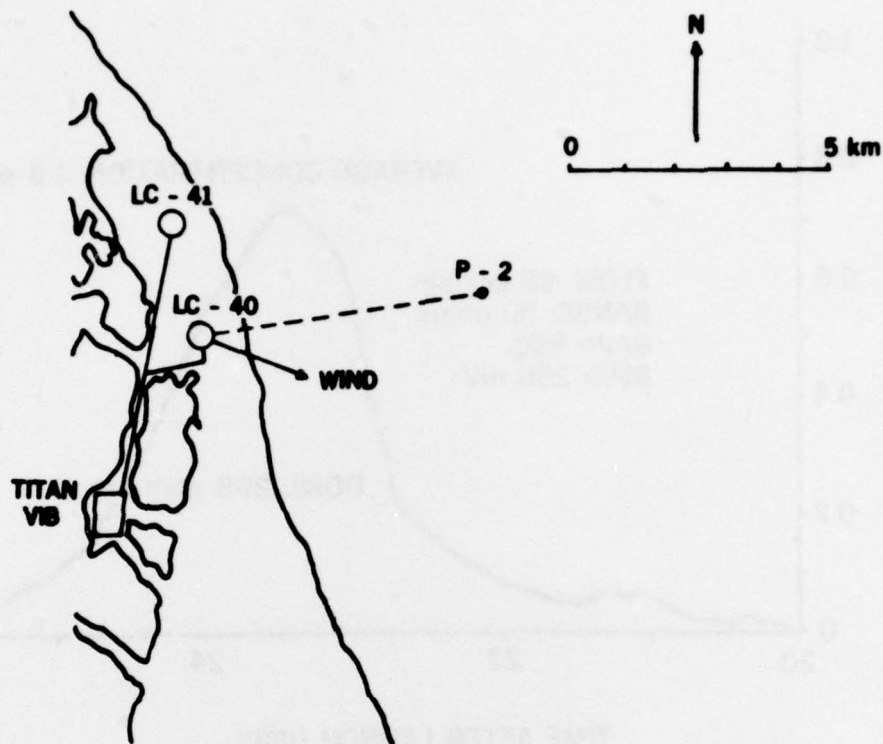


Figure 8. Sampling site of USAFSAM coulometer and chemiluminescent analyzer for the 30 May 1974 launch of a Titan IIIC at Cape Canaveral AFS.

December 1974--The fifth NASA/AF monitoring test occurred on 10 December 1974 during launch of a Titan IIIE-Centaur vehicle from LC-41, Cape Canaveral AFS, Florida. Brooks AFB personnel participated with two microcoulometers, one deployed on land and the other at sea (Fig. 10). No HCl was detected by either instrument, nor by NASA HCl detection equipment deployed concurrently at the sites.

May 1975--A 20 May 1975 launch of military communications satellites by a Titan IIIC boost vehicle was monitored by NASA and USAFSAM personnel for toxic constituents in the downwind exhaust cloud. The two USAFSAM coulometers were deployed at sea at sites P-1 and P-2 (Fig. 11). No HCl was detected by Brooks instrumentation, nor any other instruments at these sites. The operators observed the exhaust cloud passing in a southerly direction west of the two sites (toward land). Positive data were collected by at least two of the four NASA land sites (7).

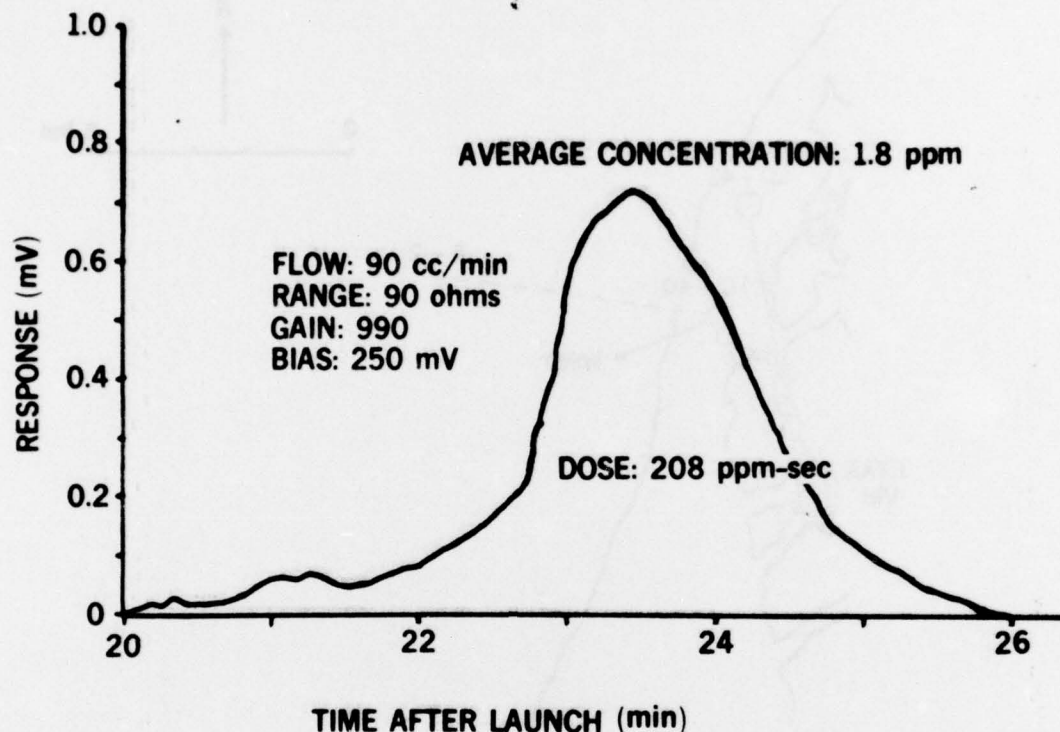


Figure 9. Coulometer trace of HCl detected on 30 May 1974 after the Titan IIIC launch at Cape Canaveral AFS.

August 1975--The first Viking A of the two-part Mars-lander program was launched on 20 August 1975 by a Titan IIIE-Centaur boost vehicle. Unstable meteorological conditions before launch forced grid placement along two predicted cloud paths, one on land and the other at sea (Fig. 12). The USAFSAM personnel and equipment were located at monitoring sites P-6 and P-7.

No HCl was detected by the coulometers nor by NASA equipment at these sites. Personnel at site P-6 observed the cloud moving to the north. Similarly, the monitors at P-7 watched the cloud split into two segments, one moving north of their position and the other south. Preliminary results showed that only one instrument, a lone chemiluminescent HCl monitor deployed in a truck (P-10) at launch, recorded positive data.

September 1975--The Viking B Mars-Lander was launched by a Titan IIIE-Centaur boost vehicle on 9 September 1975. HCl measurements were again made by both USAFSAM microcoulometers, and by the full complement

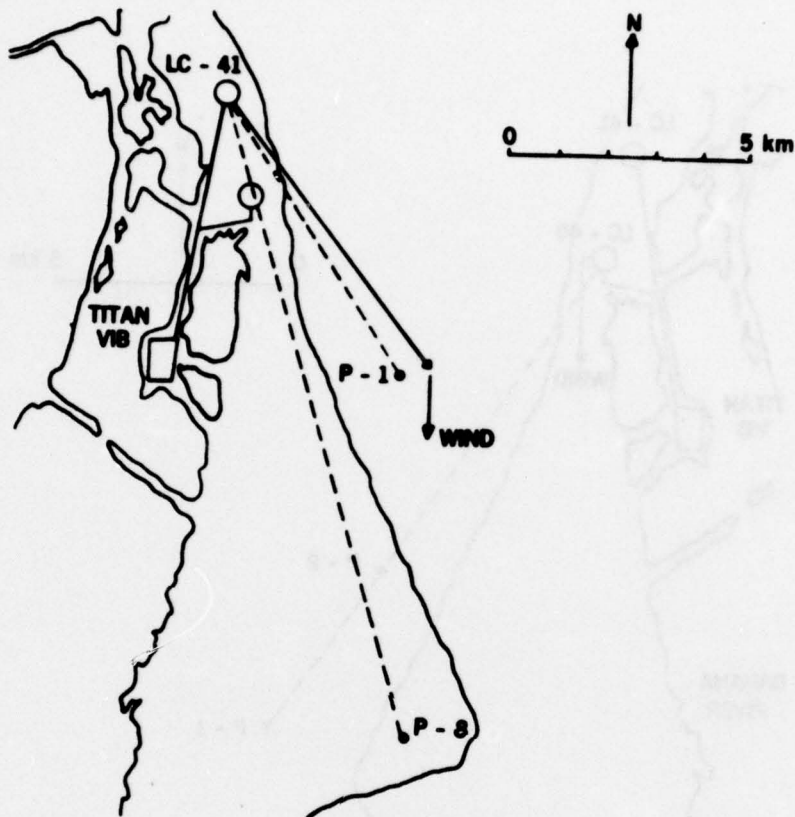


Figure 10. Sampling sites of USAFSAM coulometers for the 10 December 1974 launch of a Titan IIIE-Centaur at Cape Canaveral AFS.

of NASA instruments at 8 of the 9 primary sites. Overcast and rain threatened the launch with slight-to-heavy precipitation interfering with post-launch cloud travel and data collection. The USAFSAM micro-coulometers were located at sites P-6 and P-7 (Fig. 13). At T+16 minutes, one minute before the predicted cloud arrival, the coulometer at P-6 recorded an average concentration of 0.13 ppm ( $0.21 \text{ mg/m}^3$ ) for 5.3 minutes. The total dose of 42 ppm-sec of HCl was detected.

The coulometer at P-7 detected HCl at T+73 minutes, just as instructions were received to begin shutdown because of an impending thunderstorm. Chloride titration yielded a total dose of 480 ppm-sec of HCl and an average concentration of 4.0 ppm ( $6.5 \text{ mg/m}^3$ ). Figure 14 shows the response of the microcoulometer at site P-7.



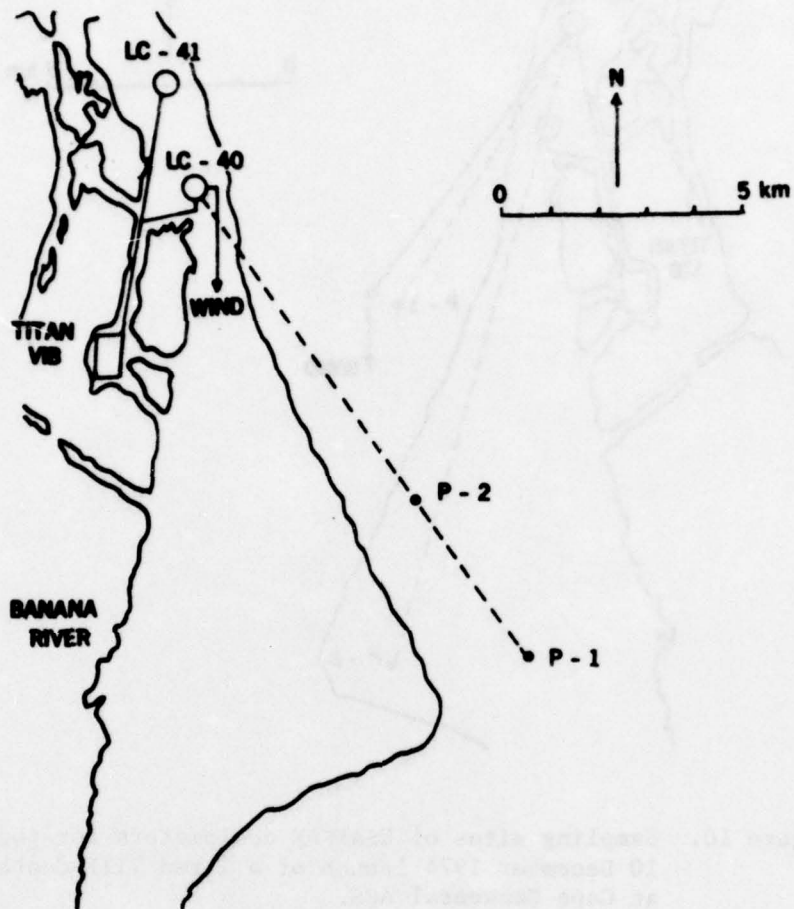


Figure 11. Sampling sites of USAFSAM coulometers for the 20 May 1975 launch of a Titan IIIC at Cape Canaveral AFS.

We postulate that the 4.0 ppm HCl (gas) concentration detected by the coulometer was washed down by rain, possibly from the ground cloud or perhaps from portions of the exhaust higher in the troposphere. The inlet to the coulometer was shielded from direct rainfall throughout the measurement period.



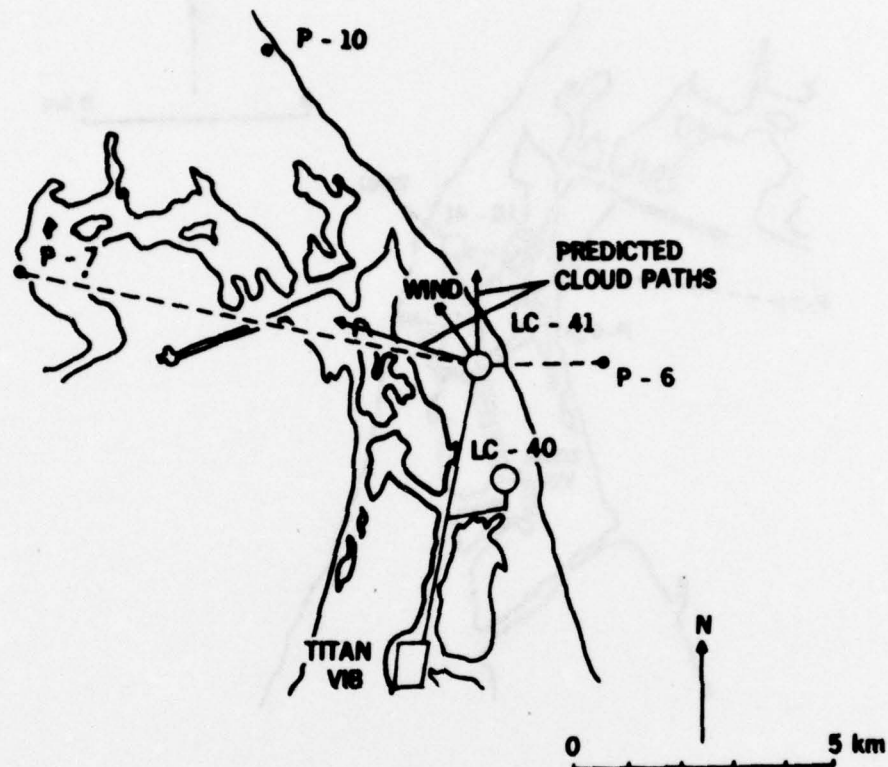


Figure 12. Sampling sites of USAFSAM coulometers for the 20 August 1975 launch of a Titan IIIE-Centaur at Cape Canaveral AFS.

#### Vandenberg Air Force Base

Background--The USAF School of Aerospace Medicine provided instrument development and monitoring assistance to the Space and Missile Test Center in support of SAMTEC-TN-10-72-001. Our primary objective was to develop analytical tools to obtain accurate measurements of HCl in the ground cloud. Secondary objectives were to validate diffusion estimates to aid in answering biomedical questions on the potential hazard of HCl in both gas and aerosol form, and on biological synergism which might obtain in HCl and alumina particulate combined to any significant degree. A threefold instrumental approach was proposed. First, the microcoulometer was repackaged for helicopter monitoring to obtain average cloud concentration of total chloride. Secondly, a fast-response chemiluminescent analyzer was developed to determine cloud concentration of HCl.

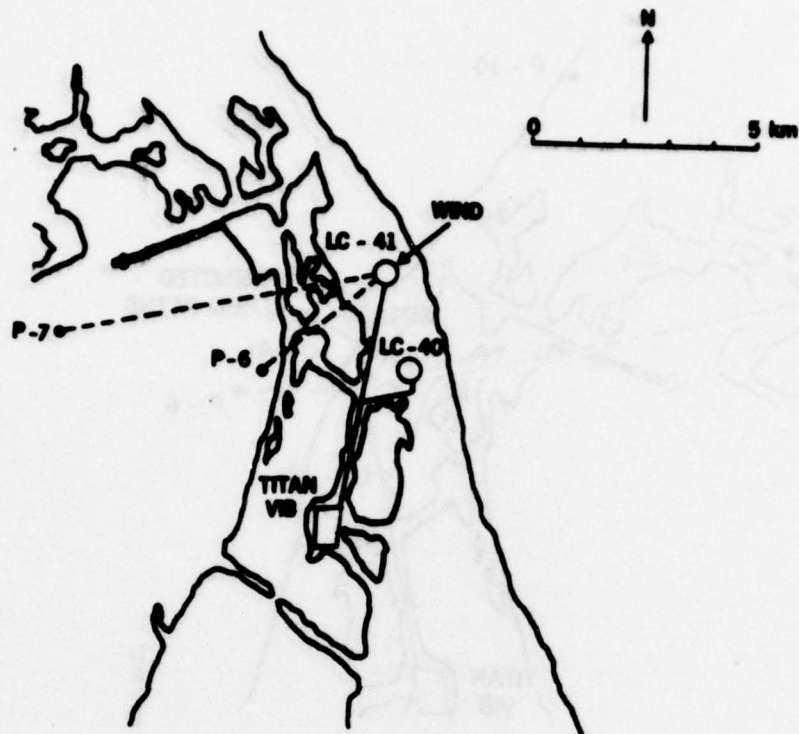


Figure 13. Sampling sites of USAFSAM coulometers for the 9 September 1975 launch of a Titan IIIE-Centaur at Cape Canaveral AFS.

Thirdly, a breadboard gas filter correlation (infrared) spectrometer was developed as an alternative instrument for measurement of gas phase HCl (1). The microcoulometer and chemiluminescent analyzers were successfully test flown in a helicopter as indicated below. The infrared detector, although conceptually adequate, proved unstable in laboratory trials and will require further development before flight test is feasible.

November 1973--The USAFSAM participated with SAMSO/SAMTEC and the Jet Propulsion Laboratory in monitoring exhaust effluents from a Titan IIID launch at Vandenberg AFB on 10 November 1973. The USAFSAM contributed a repackaged microcoulometer adapted for continuous analysis of HCl. The sampling platform was a UHIN helicopter from the Air Force Flight Test Center, Edwards AFB, California. In successive penetrations of the ground exhaust cloud, the microcoulometer made continuous measurements of HCl concentration, in conjunction with SAMTEC deployment of pH-sensitive papers.

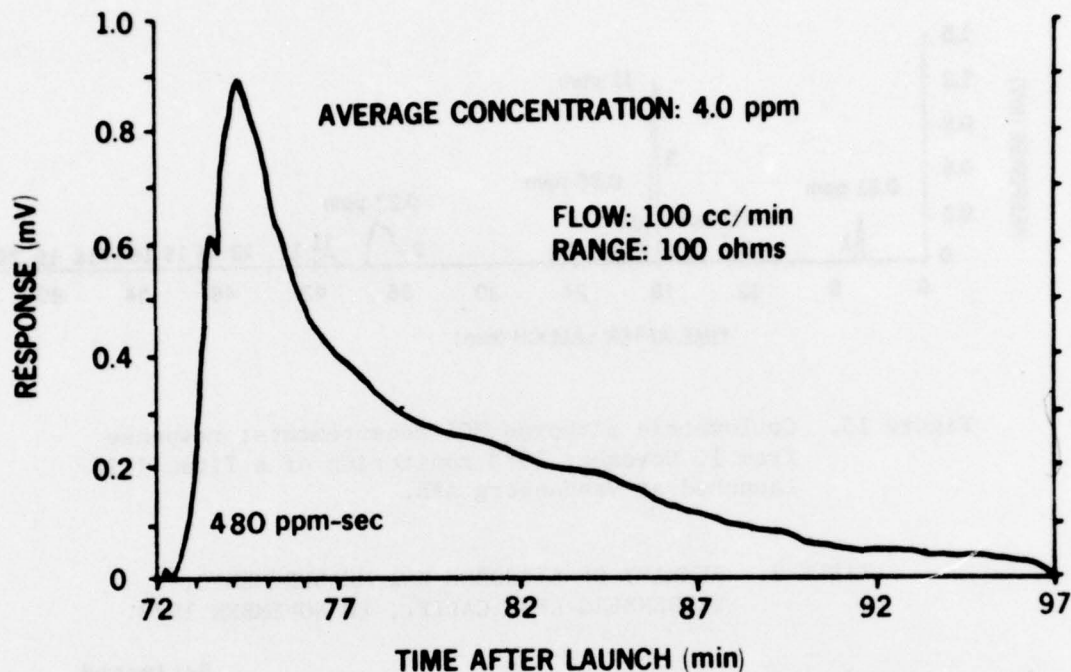


Figure 14. Coulometer trace of HCl detected on 9 September 1975 after the Titan IIIIE-Centaur launch at Cape Canaveral AFS.

During the 58-minute mission, the helicopter made 20 separate penetrations of what was assumed to be the exhaust cloud. The first penetration was made at 4 minutes after launch (T+4) and the last at T+58 minutes. Figure 15 shows a computerized reproduction of the microcoulometer response as a function of time-of-flight. The numbers 1 through 20 along the abscissa indicate cloud penetration. Table 2 summarizes the HCl dosage and average concentration determined by the microcoulometer for each of the 12 passes where positive response was obtained. Average concentration was calculated by assuming HCl was admitted only during peak (titration) rise (or the first titration rise, in the case of multiple peaks).

The maximum average concentration of 11 ppm was observed during pass No. 5, at T+18 minutes, and an altitude of about 3000 ft (914 m). The maximum dosage, of 67 ppm-sec, however, was observed during penetrations No. 6 and 7 at T+20 minutes. Translation of the dosage values to the ground contact/human exposure situation requires adjustment for the relative speed of the helicopter and the prevailing wind; i.e., assuming a 3-knot



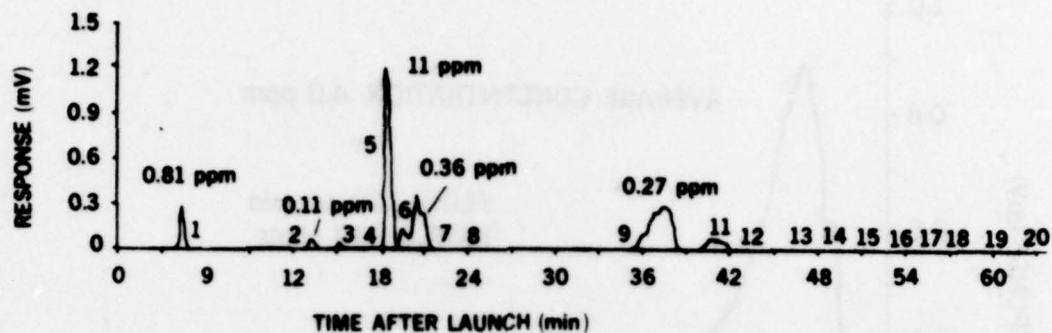


Figure 15. Coulometric airborne HCl measurements; response from 10 November 1973 monitoring of a Titan IIID launched at Vandenberg AFB.

TABLE 2. SUMMARY OF AIRBORNE HCl MEASUREMENTS, VANDENBERG AFB, CALIF., 10 NOVEMBER 1973

Peak No.	Time from launch (min)	Altitude (ft) <sup>a</sup>	HCl dosage (ppm-sec)	Estimated concentration (ppm)
1	4	1700	18	0.81
2	11	1800	5.9	0.11
3	15	1400	1.3	0.11
5	18	3000	52	10.6
6-7	20	3700	67	0.36
9	35	6400	53	0.27
10-11	39	6200	11	0.17

<sup>a</sup>To convert feet to meters, multiply by .3048.

wind velocity, the dosage measured at a 60-knot sampling speed must be increased by a factor of 60/3 or 20, to obtain the corresponding stationary point dosage. The concentration estimates can be translated with no adjustment. The validity of any translation is problematic, however, since the cloud was seen to rise throughout the 1-hour mission.

The coulometer was positioned on the left side of the helicopter behind the copilot seat. Sampling was accomplished through a 15-cm Pyrex glass tube inlet extending horizontally through the left door of the helicopter (90° to the air stream). Sample flow rate was 93 cc/min.

Operating conditions for the coulometer were: bias - 250 mV; gain - 970; and range setting (sensitivity) - 50 ohms initially, later increased to 90 ohms when HCl concentration diminished. The coulometer was operated in the continuous sampling mode throughout the mission except for two brief periods following penetrations 1 and 5 (Fig. 15). During both these passes, it was visually determined that the HCl concentration might exceed the dynamic limit of the coulometer (about 8 ppm) and sampling was temporarily discontinued to permit titration of the already admitted sample.

The results of this first monitoring test were useful to establish feasibility of the microcoulometric approach. Several operational problems were encountered during the mission which compromise the early data. First, the coulometer inlet line was not passivated prior to flight which may have caused sample loss due to wall absorption during the first several cloud penetrations. Secondly, variations in sample flow were noted during the first 10 minutes of test, but stabilized after pass 3. Thirdly, the overcast weather conditions at launch time rendered differentiation of the exhaust cloud extremely difficult, particularly in the latter part of the mission. Certainly the data collected after T+17 minutes were from pockets of (assumed) exhaust found at altitude above 2500 ft (762 m) which was above the estimated inversion layer.

April 1974--An airborne monitoring test was attempted during launch of a Titan IIID at Vandenberg AFB on 10 April 1974. This test was canceled at the last minute due to failure of the No. 2 engine on the helicopter. No data were obtained.

October 1974--The second airborne monitoring test was conducted on 29 October 1974 during launch of a Titan IIID vehicle from Vandenberg Air Force Base. The equipment deployment was identical to that of November 1973. However, care was taken in this test to passivate the coulometer inlet by frequent injection of gaseous HCl samples up to 5 minutes before takeoff. The flight plan again called for multiple penetrations of the exhaust cloud for as long as it remained a visible entity.

The results of the October 1974 test are summarized in Table 3 by cloud penetration where visual confirmation obtained (first pass only), and by individual instrument response thereafter. The results are given for each peak in terms of HCl dosage and estimated HCl concentration. Figure 16 shows a computerized reproduction of the coulometer response as a function of flight time.

The results correlate well with the November 1973 test although somewhat higher HCl concentrations were observed which prevailed for a longer period of time. However, these were mainly small tufts of exhaust found at altitudes above 3000 ft (914 m), and were probably not part of the "ground" cloud.

TABLE 3. SUMMARY OF AIRBORNE HCl MEASUREMENTS,  
VANDENBERG AFB, CALIF., 29 OCTOBER 1974

Peak No.	Time from launch (min)	Altitude (ft) <sup>a</sup>	HCl dosage (ppm-sec)	Estimated concentration (ppm)
1	1	500	28	11
2	4	1250	350	30
3	9	3500	5	2
4	10	3500	96	19
5	10	3500	26	7
6	11	3500	30	9
7	11	3600	22	6
8	13	3700	9	0.4
9	15	4500	8	0.6
10	16	4600	29	11
11	17	4800	10	5
12	19	5400	3	1
13	24	6600	5	1
14	25	6600	2	0.2
15	28	6500	3	1
16	29	6400	3	0.2
17	38	5700	100	16
18	38	5700	78	16
19	39	5700	4	2
20	42	6000	39	1
21	44	5200	106	2
22	48	4800	28	1
23	50	4600	26	-
24	56	4300	38	8
25	56	4300	51	10
26	57	4300	15	5
27	58	4300	3	1
28	59	4300	16	3

<sup>a</sup>To convert feet to meters, multiply by .3048.

Pursuit of the planned mission profile was, in fact, largely negated by a fog bank which rolled in from the ocean at about T+5 minutes, and almost totally obscured the visible exhaust cloud. Hence, the decision was made, in flight, to climb above the fog bank and monitor the visible patches of exhaust.

At several times during this mission, the microcoulometer exhibited anomalous behavior which has not been satisfactorily reproduced. The microcoulometer gave an excessively late response to the first two exhaust cloud penetrations at T+2 and T+3 minutes respectively at 1250 ft (381 m) altitude. These two successive passes were visually well defined and noted by the flight crew. The microcoulometer gave a single



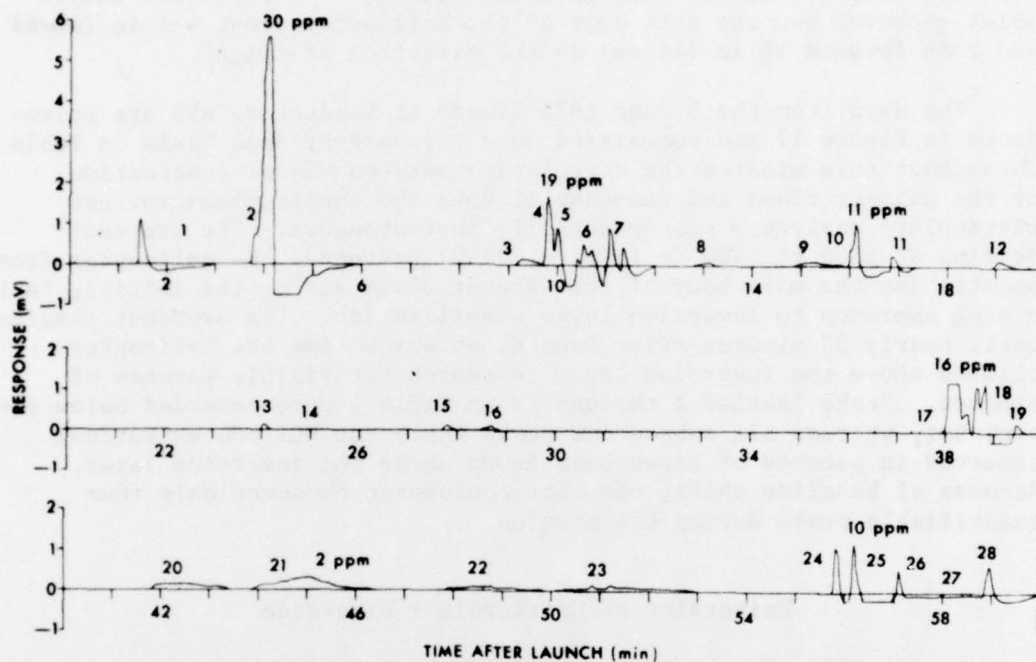


Figure 16. Coulometric airborne HCl measurements; response from 29 October 1974 monitoring of a Titan IIID launched at Vandenberg AFB.

combined response (peak No. 2 in Figure 16) at about T+14 minutes. A second anomaly observed in several responses was an atypical fast decay and undershoot of the coulometric titration curve. Examples in Figure 16 include peaks 2, 6, 10, 18, and 25. Possible explanations for this behavior include power surge, intermittent electrical short, and/or electrolyte displacement in the titration cell due to aircraft vibration and/or banking. The anomalies have not been successfully reproduced in the laboratory although several suggested causes have been eliminated (e.g., radio interference, large HCl dosage, and/or particulate interference). In any case, the concentration values (Table 3) for these response peaks were calculated by neglecting the undershoot area beneath the baseline, and hence may be in error.

June 1975--A third airborne monitoring test of a Titan IIID launch was conducted at Vandenberg AFB on 8 June 1975. For this test the sampling platform was modified by the addition of a fast-response chemiluminescent HCl analyzer (Geomet Model 402B), four-channel magnetic tape

recorder (Tandberg Series 115), and new sample inlet system. The magnetic tape recorder was employed to record data from the microcoulometer, chemiluminescent and (JPL) particulate analyzers, as well as a simultaneous voice record for ease of data reduction. The revised sample inlet extended out the left door of the helicopter about 4-6 in (10-15 cm) and then forward 18 in (46 cm) in the direction of flight.

The data from the 8 June 1975 launch at Vandenberg AFB are reproduced in Figure 17 and summarized on a response-by-peak basis in Table 4. Throughout this mission the correlation between visual penetration of the exhaust cloud and response of both the chemiluminescent and particulate analyzers was essentially instantaneous. The overcast ceiling of 1300 to 1400 ft (396 to 427 m) prevented the helicopter from penetrating the main body of the exhaust cloud during the initial, fast-rising approach to inversion layer stabilization. The overcast remained until nearly 30 minutes after launch, at which time the helicopter climbed above the inversion layer to search for visible patches of exhaust. Peaks labeled 1 through 13 in Table 4 were recorded below the overcast, whereas all subsequent peaks represent HCl concentrations observed in patches of brown haze found above the inversion layer. Because of baseline shift, the microcoulometer produced only four quantifiable peaks during the mission.

#### University of California - Riverside

August 1974--The USAFSAM provided HCl monitoring assistance to the University of California, Riverside (UCR), Statewide Air Pollution Research Center, in conjunction with Contract F33615-73-C-4059 with the Aerospace Medical Research Laboratory, Wright-Patterson AFB, Ohio. During a 21 August 1974 visit to UCR, a USAFSAM microcoulometer was employed to determine HCl buildup and decay in experimental growth chambers used to expose ornamental plants to various concentrations of missile exhaust products. Results of these studies have been reported by Lerman et al. (11).

September 1975--A second two-day series of tests was conducted at UCR on 23-24 September 1975, to validate the UCR method of analysis for HCl in plant exposure chambers. UCR employed an automatic chloride titrator to determine HCl content of bubbler samples collected in dilute nitric acid. The USAFSAM compared this method against a continuous HCl chemiluminescent analyzer (Geomet Model 401B) drawing sample directly from the plant exposure chamber.

Comparison of the measurement methods was done at five HCl concentrations in the plant exposure chamber. A schematic of the test setup is shown in Figure 18. A given concentration was obtained in the chamber by syringe pump injection of hydrochloric acid into a heated air stream which entered the chamber via an internal manifold. At each HCl concentration, chemiluminescent measurements were made by averaging three 1-minute readings, while the impinger collected a 15-, 30-, or 60-liter air sample for analysis by automatic chloride titration.

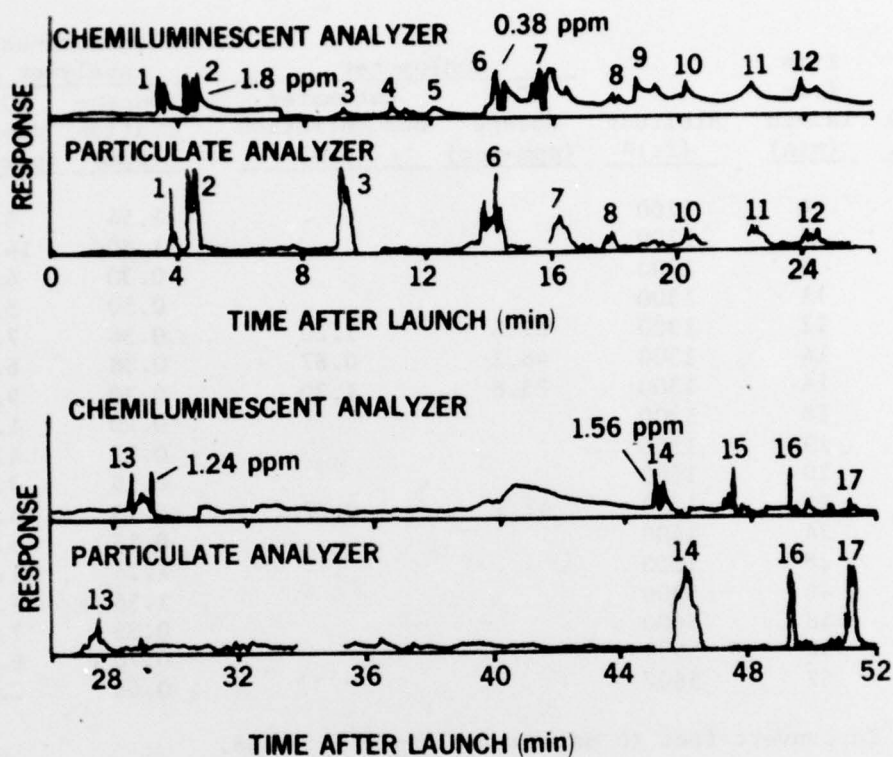


Figure 17. Chemiluminescent HCl analyzer vs JPL particulate analyzer; response from 8 June 1975 airborne monitoring of a Titan IIID launched at Vandenberg AFB.

The results of the comparison are shown in Figure 19. Agreement between the two methods was within the limits of experimental error. The chemiluminescent analyzer was prestandardized against the chloride titrator using a steady but unknown concentration of HCl in nitrogen supplied by an oven calibration system (A.I.D. Model 309). Four calibration runs were made during the two days of experiments. With the same flow conditions on the calibration delivery oven, the chemiluminescent analyzer gave a response of  $3.36 \pm 0.30$  volts to a titrator measured concentration of  $4.22 \pm 1.24$  ppm (by volume) HCl (Table 5).



TABLE 4. SUMMARY OF AIRBORNE HCl MEASUREMENTS,  
VANDENBERG AFB, CALIF., 8 JUNE 1975

Peak No.	Time from launch (min)	Altitude (ft) <sup>a</sup>	Coulometer		Chemiluminescent analyzer	
			HCl dosage (ppm-sec)	Estimated concentration (ppm)	Concen- tration (ppm)	HCl dosage (ppm-sec)
1	4	1200			1.54	5.8
2	5	1200			1.80	14.6
3	9	1300			0.30	4.2
4	11	1300			0.50	5.9
5	12	1300	67.6	1.20	0.36	7.9
6	14	1300	48.1	0.87	0.38	6.5
7	16	1300	73.8	1.30	0.30	9.7
8	18	1300			0.10	1.7
9	19	1300			0.17	4.3
10	20	1300			0.15	2.5
11	22	1350	42.1	0.77	0.15	4.6
12	24	1400			0.15	5.3
13	28	1850			1.24	31.1
14	46	5300			1.56	17.8
15	48	5600			0.36	7.8
16	50	5600			0.70	6.8
17	52	5600			0.66	2.9

<sup>a</sup>To convert feet to meters, multiply by .0348.

#### Naval Weapons Center - China Lake

In August-September 1974, the USAFSAM participated with NASA/Langley Research Center, SAMTEC, and NWC in monitoring HCl in the ground exhaust cloud from static test of small rocket motor firings at the Naval Weapons Center, China Lake, Calif. A group of 22, 8-lb (18-kg) solid rocket motors (SRM) were fired vertically downward from a 20-ft (6-m) tripod, for three purposes: (1) instrument comparison between the coulometer (USAFSAM), chemiluminescent analyzer (NASA), pH recorder (SAMTEC) bubblers (NASA), and silver nitrate indicator tubes (NWC); (2) source term measurements with the instruments located in concentric circles around the firing stand; and (3) diffusion measurements with the instruments located in a pie-shaped sampling grid downwind of the firing stand. Six motors were fired for instrument comparison, 5 for source term measurements, and 11 for diffusion tests. Results of the instrument comparison showed good agreement between the two coulometers in terms of total dose (ppm-sec); two chemiluminescent analyzers indicated good agreement on maximum concentration but a wider standard deviation on total dose. The pH recorders showed wide deviation in both concentration (based on slope) and dose (based on area). The source term measurement tests showed maximum concentrations of approximately 130 ppm HCl for those

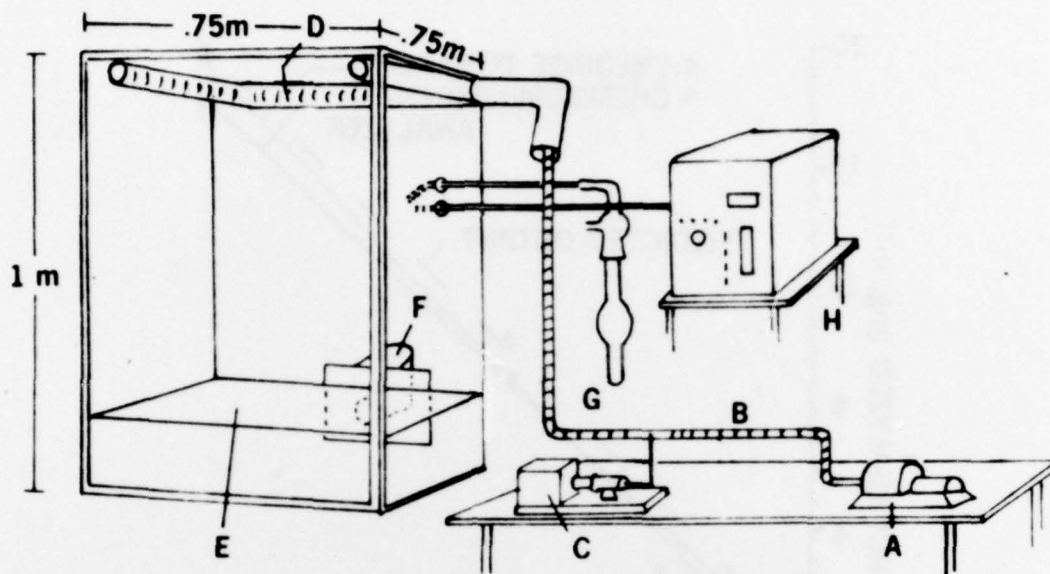


Figure 18. UCR plant exposure chamber: A. compressor; B. heated line; C. syringe pump for HCl injection; D. dispersion manifold; E. perforated base; F. high-volume exhaust motor; G. bubbler for HCl collection in dilute nitric acid; H. chemiluminescent HCl monitor.

detectors located very close to the centerline of cloud travel and less than 25 m from the test stand. The diffusion test data, although somewhat limited, provided one network for scaling of meteorological models from small-to-medium and full-scale launch predictions. Detailed results of the phase I and II studies have recently been published by Nadler (13). The phase III diffusion studies were sponsored by NASA and will be reported in a separate publication.

#### Marshall Space Flight Center - Huntsville

Background--In order to broaden the data base for validation of the NASA multi-layer diffusion model, the USAFSAM conducted HCl measurements of the exhaust cloud from a series of static tests conducted at the Marshall Space Flight Center (SFC), Huntsville, Alabama. The test firings were designed primarily to assess the effect of flame-bucket geometry on environmental noise pollution from the space transportation

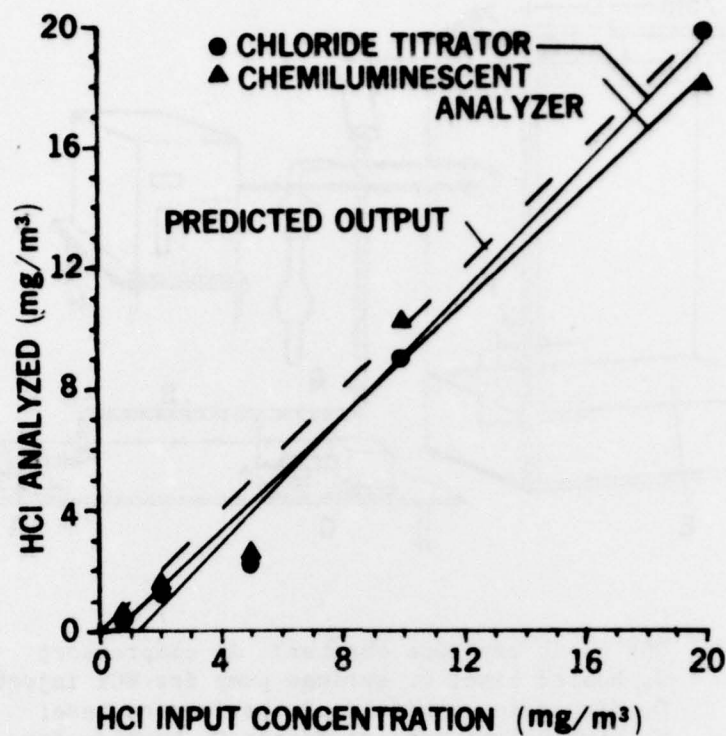


Figure 19. UCR chloride titrator vs chemiluminescent HCl monitor (Model 401B).

TABLE 5. CHEMILUMINESCENT HCl ANALYZER CALIBRATION DATA, UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIF., 23-24 SEPTEMBER 1975

Date/time	Chemiluminescent analyzer response (volts)	Chloride titrator concentration	
		ppm	mg/m <sup>3</sup>
23 Sep/morning	3.25	2.6	4.2
23 Sep/afternoon	3.10	5.2	8.4
24 Sep/morning	3.80	3.9	6.3
24 Sep/afternoon	3.30	5.2	8.5
Average	3.4±0.3	4.2±1.2	6.9±2.0



system (space shuttle). The test vehicle was a 6.4% scale model of the shuttle launch configuration (liquid-fueled center engine plus two solid-fueled strap-on boosters). The HCl-monitoring program was ancillary to the main acoustic measurements, and was a cooperative effort with the Arnold Engineering Development Center, funded by NASA.

February 1975--On 8 February 1975, the first HCl measurement test was made using a USAFSAM microcoulometer and chemiluminescent analyzer, deployed 15 m apart, 150 m downwind of the test stand as shown in Figure 20. Since the shuttle launch pad deflects solid motor exhaust 180° from the liquid motor exhaust, the instrument deployment was optimized to detect the solid exhaust (within the constraints imposed by availability of electrical power).

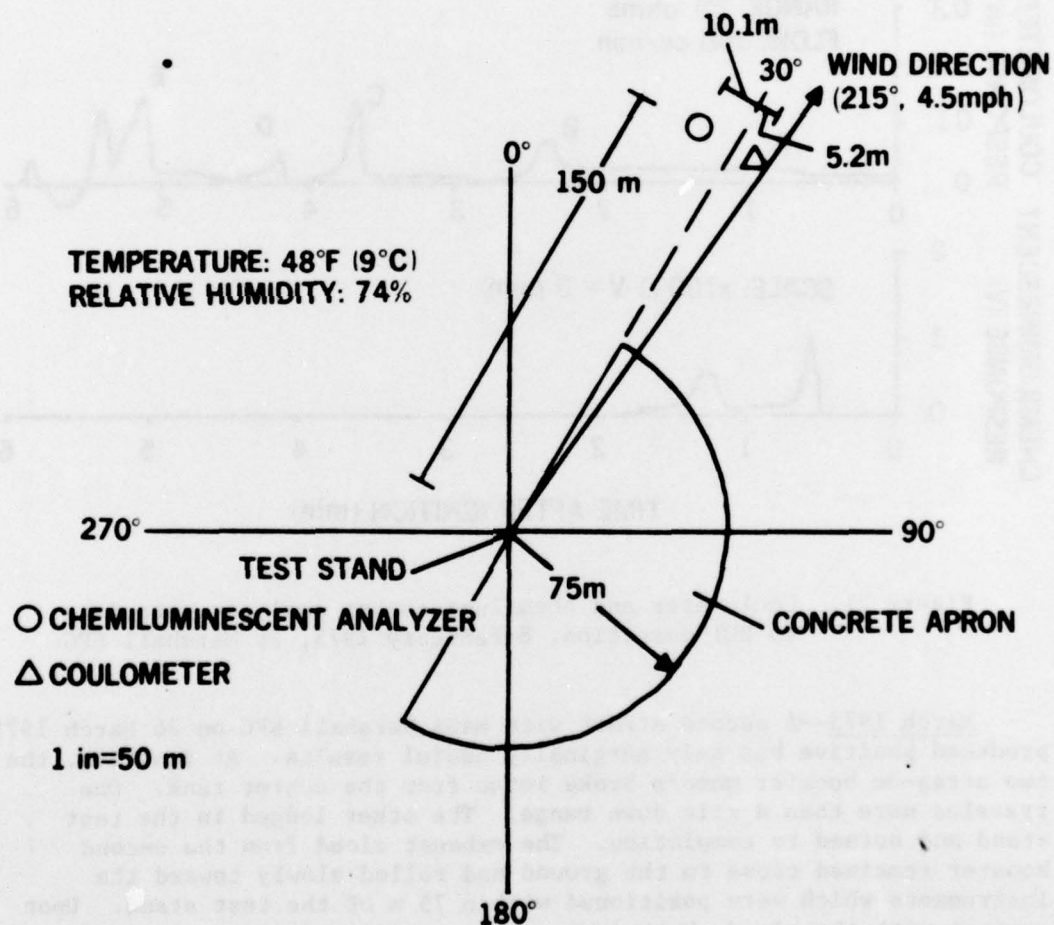


Figure 20. Instrument placement diagram of test fire, 8 February 1975, at Marshall SFC.

The instruments' responses are shown in Figure 21 for the time interval from T-0 to T+6 minutes. A summary of the diffusion measurements is in Table 6. These results represent only trailings from the buoyant exhaust cloud as it passed over the instrument site. Sequence photos showed that by T+10 seconds the main body of the cloud had begun to rise while only 100 m downwind from the test stand. At T+20 seconds the visible cloud was well off the ground (10 m) and continuing to rise as it passed over the instruments. At no point did the main body of the moving cloud come in contact with the instruments.

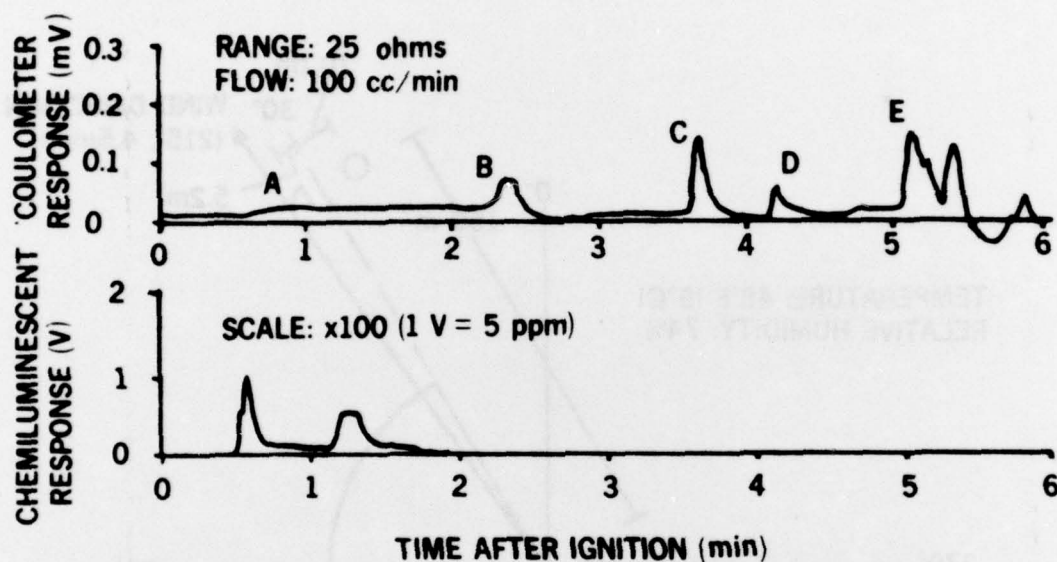


Figure 21. Coulometer and chemiluminescent analyzer responses to HCl detection, 8 February 1975, at Marshall SFC.

March 1975--A second effort with NASA Marshall SFC on 26 March 1975 produced positive but only marginally useful results. At ignition, the two strap-on booster motors broke loose from the center tank. One traveled more than a mile down range. The other lodged in the test stand and burned to completion. The exhaust cloud from the second booster remained close to the ground and rolled slowly toward the instruments which were positioned within 75 m of the test stand. Upon contact with the cloud, both instruments registered off-scale readings, thereby enabling us to report only that the concentration was greater than 50 ppm. This concentration represents the dynamic limit of the chemiluminescent analyzer.

TABLE 6. SUMMARY OF HCl DIFFUSION MEASUREMENTS,  
MARSHALL SFC, ALABAMA, 8 FEBRUARY 1975

<u>Coulometer</u>				
<u>Response</u>	<u>Time (min)</u>	<u>HCl dosage (ng)</u>	<u>Concentration (ppm)</u>	
			<u>Steady state</u>	<u>Dose/Vol</u>
A	1.0	- <sup>a</sup>	0.06	-
B	2.4	8.2	0.40	0.59
C	3.7	18.2	- <sup>b</sup>	2.1
D	4.2	4.6	-	1.6
E	5.1	15.9	-	2.7

<u>Chemiluminescent analyzers</u>			
<u>Response</u>	<u>Time (min)</u>	<u>Concentration</u>	
		<u>(ppm)</u>	
F	0.6	5.0	
G	1.2	3.0	

<sup>a</sup>The area under the curve was too small for measurement.

<sup>b</sup>The steady state was not achieved.

#### DISCUSSION AND CONCLUSIONS

The field test program to date has provided a clear indication of instrumentation preference for specific applications, but only preliminary insight into the behavior of the exhaust cloud following rocket launch. The detection concept and fast-response characteristics of the chemiluminescent analyzer make it clearly superior for the airborne-monitoring application. The coulometer by contrast has proved itself as a versatile laboratory tool and a useful field instrument for HCl detection in ground-monitoring applications. The fact that the coulometer is a primary standard for total chloride analysis alleviates the time-consuming and difficult task of field calibration. The principal disadvantages of the coulometer are its slow time of response and somewhat limited dynamic range, which are of minor concern in the low-level relatively slow exposure situation encountered in ground monitoring. In comparison, the chemiluminescent analyzer gives an instantaneous response to gaseous HCl which is highly advantageous for airborne measurement. The chief disadvantage of the chemiluminescent approach is that it is not a standard for measurement of HCl gas but must be calibrated with a known concentration or referee method. This disadvantage is partially compensated by the fact that the chemiluminescent response is linear with HCl concentration which normally permits single-point calibration. Where logistics allow, the use of both instruments is advantageous since the microcoulometer measures total chloride and the chemiluminescent analyzer is specific for gaseous HCl.



With respect to cloud behavior, the USAF data base is somewhat meager and subject to conflicting interpretation. On the one hand, none of the airborne or downwind surface levels have exceeded the short-term public limit of 4 ppm for 10 minutes recommended by the National Academy of Sciences. Overall, the measured HCl concentrations have tended to be lower than predicted by diffusion modeling. This finding is an essential agreement with the more extensive results from the NASA program at Cape Canaveral (7). Translation of Eastern Test Range data to Vandenberg AFB, however, must be done with due consideration of the climatic and topographic differences. On the other hand, instantaneous concentrations at or above 4 ppm have been measured as long as 50 to 60 minutes after launch at altitudes above the inversion layer, 5-15 miles (8-24 km) from the launch site. The emerging picture on exhaust cloud behavior at Vandenberg is one of generalized downwind drift with slow disintegration into segments, rather than bulk diffusion of a single entity. The cloud segments, although individually small, may contain relatively high concentrations of HCl in gaseous form. However, these high measurements have been predominantly at altitudes above the prevailing overcast and therefore presumably above the inversion layer. The data collectively neither support nor refute the return of the "ground" cloud to the surface, as predicted or assumed in diffusion modeling.

In terms of data collection, there appears little doubt that airborne monitoring has been more cost effective than ground measurements at Cape Canaveral. Although the prevailing overcast at Vandenberg AFB has, in part, compromised each mission, the mobile sampling platform nonetheless provides opportunity for multiple penetrations of the exhaust cloud and thus greatly increased chance for data collection. The use of helicopter side inlets for airborne sampling is somewhat problematic because of the adverse influence of rotor turbulence. Sampling of the undisturbed cloud can be done more effectively with nose-mounted inlet probes on either a helicopter or small fixed-wing aircraft. In a joint sampling effort with the U.S. Environmental Protection Agency, we observed excellent correlation between the microcoulometer and chemiluminescent analyzers using nose sampling from a Beech C-45 aircraft to monitor the exhaust plume from the incinerator ship Vulcanus (12). We recommend that any future HCl sampling studies at Vandenberg AFB incorporate both the microcoulometer and chemiluminescent analyzers in an airborne platform with nose-sampling capability.

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